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## (54) "OXIDATION CATALYST AND ITS USE"

- (71) We, CHEVRON RESEARCH COMPANY, a corporation duly organized under the laws of the State of Delaware, United States of America, of 200 Bush Street, San Francisco, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved hydrocarbon oxidation catalyst especially suitable for use with saturated hydrocarbon feeds. More particularly, it relates to improved vanadium oxide-phosphorus oxide composites. Still more particularly, it relates to the production of maleic anhydride from n-butane in a vapor phase process employing the foregoing catalyst.

It is known in the art that n-butane can be used as a feed for the production of maleic anhydride. n-Butane is available from petroleum refinery streams and is a relatively inexpensive feed for a maleic process. Nevertheless, there is little or no use of n-butane as a process feed for the production of maleic anhydride. Why is this? It appears that known catalysts for the partial oxidation of n-butane are unsatisfactory. A very active catalyst is required for the oxidation. Yet this very characteristic tends to be incompatible with the requirement that the oxidation be a selective partial oxidation rather than a total oxidation to carbon oxides. That is to say, presently known catalysts for the oxidation of n-butane to maleic anhydride have, in general, relatively poor selectivities.

Representative descriptions in the art which relate to the production of maleic anhydride from n-butane include U.S. Patent No. 3,293,268.

In accordance with the present invention a catalyst having excellent activity and improved selectivity in the oxidation of n-butane to maleic anhydride has now been found. It is a crystalline composite or complex of vanadium-oxide and phosphorus oxide which has:

- 1) an intrinsic surface area of the mixed oxide per se in the range from about 7 to 50 square meters per gram;
- 2) a phosphorus to vanadium atomic ratio in the range 0.9-1.8 to 1, respectively;
- 3) a vanadium oxide component having an average valence for vanadium in the range plus 3.9 to 4.6; and
- 4) a phosphorus oxide component having an average valence for phosphorus of plus 5.

By intrinsic surface area of the mixed oxide, as used in this description, is meant the surface area of the material itself, i.e. per se, and in the absence of a support or carrier.

The novel crystalline compositions herein are prepared by formation of a vanado-phosphato mixed oxide complex in an essentially organic solvent medium. A minor amount of water may be present in the medium and indeed water or water-forming components bound in the precipitate are believed to be required in order to obtain a catalyst having a satisfactory selectivity and activity. The presence of a gross amount of water in the medium during the crystal-forming precipitation prevents the formation of the present novel mixed oxide catalysts having a relatively high intrinsic

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surface area. The isolation of the mixed oxide may be effected by evaporation of the organic solvent. The resulting crystalline solid is freed of solvent, and is then activated by heating in air for use as an oxidation catalyst. The activation procedure is required to condition the precipitated and dried mixed oxide (i.e., it is a catalyst precursor) for use as an oxidation catalyst. During the activation bound water (apparently water of hydration), or a mixture of water and organic solvent is evolved and a crystal phase change occurs.

In a preferred method for the preparation of a crystalline vanado-phosphato mixed oxide of the invention comminuted vanadium pentoxide ( $V_2O_5$ ) and isobutanol are charged to a glass lined reactor fitted for stirring, temperature control, the introduction of a gas into the isobutanol and for the exclusion of water vapor. For each formula weight in grams of the vanadium pentoxide, about 1 liter of the isobutanol solvent is used. The resulting slurry is then stirred and the vanadium pentoxide is dissolved in the isobutanol by passing a stream of anhydrous hydrogen chloride gas into the slurry while maintaining the temperature between 30 and 40°C. The resulting solution is red-brown colored and nearly saturated with hydrogen chloride gas. It is ready for mixing with a solution of orthophosphoric ( $H_3PO_4$ ) acid in isobutanol.

The orthophosphoric acid solution is prepared by adding crystalline 100% orthophosphoric acid to isobutanol in a glass lined vessel large enough to accommodate the solution of vanadium oxide prepared as described above and the phosphoric acid solution. For each mol of the acid a volume of about 100 milliliters of isobutanol is desirably used. Sufficient orthophosphoric acid is charged to the vessel to yield, upon the addition of the red-brown solution of dissolved vanadium oxide, a phosphorus to vanadium atomic ratio of 1.2. The vessel should be fitted for stirring, temperature control, reflux, the introduction of the red-brown solution and for the exclusion of water vapor.

After the introduction of the red-brown solution to the phosphoric acid solution in the second vessel, the temperature of the resulting solution is increased to the reflux temperature, i.e., about 110°C., and is maintained for about 1.5 hours. Evidence of a reaction is notable in that the solution changes in color, usually to a greenish-brown. Thereafter, the reflux condenser is removed and isobutanol solvent is distilled from the reaction mixture. During the heating above at reflux and subsequently during distillation, hydrogen chloride gas evolves from the solution and is vented.

As the heating is continued and the volatiles, mainly isobutanol and hydrogen chloride, are evolved, the color of the solution continues to change; transitorily it assumes various shades of green or blue, the colorations associated with vanadium in the plus 4 valence (oxidation) state. Finally, after about two-thirds of the solvent has been evolved, the solution is colored a greenish-blue. Some light blue precipitate is usually present in the concentrate at this time. The remainder of the volatiles are conveniently removed by placing the concentrate in a loosely covered glass vessel in a ventilated oven maintained at 150°C. Drying is continued until resulting precipitated solid reaches a substantially constant weight.

The dried precipitate is a uniform, very dark green-grey solid which after activation has a surface area (BET-Method) of about 23 m<sup>2</sup>/gr. For fixed bed use it is broken up and sieved to a 20-28 mesh (Tyler Screen) size.

For the activation the following schedule is carried out:

1. Heat the precursor to 380°C. in a stream of air flowing at 1.5 volume/volume/minute. The heat input should yield a rate of temperature increase of 3°C. per minute.
2. Maintain the 380°C. temperature and the same air flow rate for 2 hours.
3. Increase the temperature from 380°C. to 480°C. at the 3°C. per minute rate of increase while passing an air-butane mixture, 1.5 volume percent of butane in air, through the bed (10 inch by 0.5 inch diameter tube) at a flow rate of 1.5 volume/volume/minute.
4. Maintain the precursor at 480°C. for about 16 hours while continuing the air-butane flow rate as before.
5. Reduce the temperature from 480°C. to 420°C. and then increase the air-butane flow rate to to VHSV of 1000 hr.<sup>-1</sup> (17 vol/vol/min.).
6. Finally adjust the temperature upward or downward as required until the butane conversion is 90%.

Usually the catalyst performance stabilizes after a short run of from 6 to 36 hours. The activated catalyst has a standard activity (see discussion below) which is generally below 400°C., usually in the range 365-390°C. and a surface area (BET) of about 23 square meters per gram. This catalyst usually produces 105 kilograms of maleic anhydride per 100 kilograms of n-butane fed to the reactor or 117 kilograms of maleic anhydride per 100 kilograms of n-butane converted.

In order to obtain a reliable comparison of oxidation catalysts herein, a standard test was required and developed. Ten milliliters of 20/28 mesh mixed oxide was charged to a one-half inch stainless steel reactor. After activation, performance was measured at a space velocity (volume at 0°C. and 1 atm/volume/hr) of 1000 hr.<sup>-1</sup> using a feed of 1.5 volume percent n-butane in air. The catalyst was left onstream until its performance changed very little over a 24-hour period.

As the index of activity, I define "standard activity" as that temperature required for 90% conversion under the above conditions. Yield is defined as pounds of maleic anhydride produced per 100 pounds of hydrocarbon fed, and selectivity as pounds of maleic anhydride produced per

100 pounds of feed converted.

Depending upon variations in the organic solvent system employed and in some degree upon the activation procedure, the intrinsic surface area [BET Method — cf., H. Brunaur, P. H. Emmett, and E. Teller, JACS., Volume 60, Page 309 (1938)] ranges from 7 to 50 square meters per gram. The preferred mixed oxide catalysts have intrinsic surface areas in the range from 10 to 50 m<sup>2</sup>/gr. In general, the higher the intrinsic surface area, the more active is the catalyst, and the lower is the temperature at which the catalyst is satisfactory for use in the oxidation of a saturated hydrocarbon feed.

The precipitated mixed oxides herein should have an atomic ratio, phosphorus to vanadium, which in general is in the range from 0.9-1.8 to 1, preferably 1.0-1.5 to 1, respectively.

The average valence of the vanadium in the activated mixed oxides of the invention is, in general, in the range from 3.9 to 4.6. Better results are believed to obtain when the average valence is in the range 4.1 to 4.4.

The selectivity of the oxidation catalysts herein was found to be directly related to the proportion of the composite which was of a particular crystal structure. For purposes of reference and since no mention or recognition of this composite structure appears to be in the art, it is designated as the B-phase. The crystals having the B-phase structure exhibit a characteristic powder x-ray diffraction pattern (CuK $\alpha$ ), as listed in Table I below:

TABLE I

<i>d (Angstrom)</i>	<i>Line Position 2<math>\theta</math>, Degrees</i>	<i>Intensity, I</i>
6.3	14.2	10
4.8	18.5	7
3.9	23.0	100
3.13	28.5	58
2.98	30.0	29
2.65	33.8	7

The dimensions of the unit cell for B-phase, as obtained from the complete powder x-ray diffraction data, are  $a = b = 19.2 \text{ \AA}$  and  $c = 7.8 \text{ \AA}$ . The crystalline phase is of hexagonal structure.

The phosphorus-vanadium mixed oxides which have a B-phase content of at least 25 percent and an intrinsic surface area in the range above 10 m<sup>2</sup>/gr. exhibit good activities and selectivities in the vapor phase partial oxidation of saturated hydrocarbon feeds. Consequently, these composites are preferred. Those having a B-phase content in excess of 50 percent exhibit, in general, excellent activities and selectivities and are most preferred. The relative amount of B-phase in a given composite is conveniently measured by the method of the National Bureau of Standards (Reference, United States Department of Commerce, N.B.S., Monograph 25, Section 6, Page 3). In the method  $\alpha$ -alumina is used as an internal standard, and the x-ray diffraction pattern for a 5:1 (weight) mixture of mixed oxide and  $\alpha$ -alumina is obtained. The ratio of the intensity (I) of the  $d = 3.9 \text{ \AA}$  line of the mixed oxide to the  $d = 2.085 \text{ \AA}$  line of the  $\alpha$ -alumina standard is a measure of the relative amount of the B-phase content for a given composite. With a sample of mixed having approximately 100% B-phase, the ratio of intensities is 3.1. If the B-phase content is 25 percent, then the ratio is approximately 0.8. The following Examples further illustrate the invention.

The mixed oxide composition herein may be prepared by a variety of reagents using a substantially organic medium. Table II below includes a number of representative reactant combinations for the preparation of vanadium-phosphorus mixed oxides. In Table IV, Examples 1-13 illustrate the use of a variety of representative organic solvents for the production of mixed oxides having a high intrinsic surface area. Examples 14-18 illustrate the effect of water upon the catalyst surface area and/or activity, Examples 14 and 18 being by way of comparison as are Examples 19 and 20 which describe catalysts prepared in the absence of a solvent.

TABLE II

<i>REACTANTS</i>	<i>DESIGNATOR</i>
1. $\text{VOCl}_3 + 1.2 \text{ H}_3\text{PO}_4 + \text{X H}_2\text{O}$	A
2. $1/2 \text{ V}_2\text{O}_5 + 1.2 \text{ POC l}_3 + \text{X H}_2\text{O}$	B
3. $1/2 \text{ V}_2\text{O}_5 + 1.2 \text{ H}_3\text{PO}_4 + \text{X H}_2\text{O} + \text{HCl}$ (excess) (a)	C

Table II continued

	4.	$\text{NH}_4\text{VO}_3 + 1.2 \text{POCl}_3 + \text{XH}_2\text{O}$	D	
5	5.	$1/2 \text{V}_2\text{O}_5 + 0.5 \text{PCl}_3 + 0.7 \text{H}_3\text{PO}_4$ + $\text{X H}_2\text{O} + \text{HCl}$ (excess) (a)	E	70
10	6.	$1/4 \text{V}_2\text{O}_3 + 1/4 \text{V}_2\text{O}_5 + 1.2 \text{H}_3\text{PO}_4$ + $\text{X H}_2\text{O} + \text{HCl}$ (excess) (a)	F	75
	7.	$\text{V}_2\text{O}_5 + \text{H}_3\text{PO}_4$ (85% concentration)	G	
15	(a)	Gaseous HCl bubbled into reactants until dissolution of $\text{V}_2\text{O}_5$ .		80

In Table III below are listed the preparative methods employed for the several combinations of reactants listed above and a designator. The two designators, a capital letter for reactants, and a numeral for method, are used to identify the mixed oxides in Table IV below.

TABLE III

		METHOD OF PREPARATION	DESIGNATOR	
25	1.	Preparing a solution, then boiling off the solvent to leave a solid mass.	(1)	90
30	2.	Preparing a solution, boiling off part of the solvent, and collecting the resulting precipitate.	(2)	95
	3.	Mixing the reactants without solvent.	(3)	
35	4.	Mixing the reactants without solvent and fusing at $900^\circ\text{C}$ . for 2 hours.		100

Examples 1-13 illustrates that a mixed oxide complex of vanadium oxide and phosphorus oxide having a relatively high intrinsic surface area, for example in the range above 7 square meters per gram, and a B-phase content above 25 percent, has an excellent activity and selectivity as a catalyst for the partial oxidation of n-butane to maleic anhydride.

## EXAMPLES 21-24:

In the manner described in the preferred embodiment, a series of mixed oxide complexes was prepared, activated, and tested except that the phosphorus to vanadium (P/V) atomic ratios of the complexes were varied as follows: 0.9, 1.0, 1.1, 1.2, 1.3, 1.5, and 1.8. The resulting comparative data for the activated catalysts is listed below in Table V.

TABLE V

	EX. NO.	ATOMIC RATIO, P/V	STD. ACTIVITY $^\circ\text{C}$ .	SURFACE AREA, $\text{m}^2/\text{gr}$ .	B-PHASE <sup>(1)</sup> %	YIELD <sup>(2)</sup> WT. %	
50	21	1.1	392	27	76	94	115
55	22	1.2	373	16	53	99	120
	23	1.3	403	20	42	87	
60	24	1.5	475	12	28	65	125

(1) By x-ray diffraction analysis.

(2) Based on butane fed at the standard activity temperature.

These examples demonstrate that both the yield and the activity of the catalyst composites are directly related to the B-phase content.

TABLE IV

EX. NO.	REACTANTS AND METHOD	MOLS WATER ADDED "X"	STANDARD CATALYST PERFORMANCE(9)				ACTIVATED CATALYST		
			SOLVENT(1)	CONV. %	TEMP. °C.	YIELD(2) WT. %	SURFACE AREA (BET, m <sup>2</sup> /g)	OXIDATION STATE OF VANADIUM	B-PHASE(10) %
1	A-1	1.2	THF(3)	90	430	104	19	4.1	88
2	B-1	3.6	THF(3)	90	408	98	18	4.2	83
3	A-1	0	THF(3)	90	420	96	22	4.1	90
4	C-1	0	Isobutanol	90	374	105	23	4.2	73
5	B-1	3.6	1,2-Dimethoxy-ethane	90	452	97	12	4.4	42
6	B-1	3.6	" (4)	90	422	89	15	-	-
7	B-1	3.6	" (5)	90	404	93	21	4.1	-
8	C-1	0	Methanol	90	468	90	8	4.3	81
9	C-1	0	Acetic Acid(6)	90	465	76	10	-	-
10	D-1	3.6	1,2-Dimethoxy-ethane	90	472	73	11	-	27
11	C-1	0	Acetic Acid(8)	90	446	73	15	-	-
12	F-1	0	ClCH <sub>2</sub> CH <sub>2</sub> Cl: Methanol: 2:1	90	446	76	10	-	-
13	B-1	3.6	Acetone	90	553	25	15	4.6	-

70

75

80

85

90

95

100

105

110

115

120

125

130

TABLE IV (continued)

EX. NO.	REACTANTS AND METHOD	MOLS WATER ADDED "X"	EFFECT OF WATER	STANDARD CATALYST PERFORMANCE <sup>(9)</sup>			ACTIVATED CATALYST		
				CONV. %	TEMP. °C.	YIELD <sup>(2)</sup> WT. %	SURFACE AREA (BET, m <sup>2</sup> /g)	OXIDATION STATE OF VANADIUM	B-PHASE <sup>(10)</sup> %
14	F-1	0	Acetic Anhydride	16	510		5	4.6	
15	E-1	0	Acetic Acid + Ac <sub>2</sub> O <sup>(7)</sup>	38	510	23	16	3.9	
16	E-2	2.0	Acetic Acid	90	399	92	15	4.2	
17	C-1	5.0	Acetic Acid: H <sub>2</sub> O = 16:3 <sup>(8)</sup>	90	424	83	11		
18	F-1	20	Propionic Acid: H <sub>2</sub> O = 2:3	49	510	42	5		40
19	G-3		None	90	532	40	3	4.1	
20	G-4		None	48	536	17		4.5	

(1) 500 mls of solvent used per gram atom of phosphorus. Solvent ratios are by volume.

(2) Based on butane fed.

(3) Tetrahydrofuran.

(4) 33 Wt. % maleic acid, based on V<sub>2</sub>O<sub>5</sub>, added.(5) 66 Wt. % bis-(2-methoxyethyl)ether, based on V<sub>2</sub>O<sub>5</sub>, added.(6) 2 mols paraformaldehyde per mol V<sub>2</sub>O<sub>5</sub>.(7) 4 mols acetic anhydride per mol V<sub>2</sub>O<sub>5</sub>.(8) 1 mol of benzaldehyde added per mol of V<sub>2</sub>O<sub>5</sub>.(9) Catalyst performance determined at a space velocity of 1,000 hrs.<sup>-1</sup> (STP) and using 1.5 volume percent of n-butane in air.

(10) As measured by x-ray diffraction.

## EXAMPLES 25-31:

Using a catalyst prepared in the manner described in the embodiment, and a space velocity of 1000 hr<sup>-1</sup>, and a feed of 1.5 volume percent hydrocarbon in air, other hydrocarbon feeds were oxidized. The feeds and results obtained are listed in Table VI below.

TABLE VI

EX. NO.	FEED COMPOUND	TEMP. °C.	CONV. %	YIELD WT. %
25	n-pentane	368	90	64
26	isopentane	380	80	56
27	methylcyclopentane	380	91	63
28	2-butene	375	99	85
29	butadiene	335	100	86
30	benzene	417	92	55
31	o-xylene	358	90	(1)
(1)	31% phthalic plus 8% maleic anhydride.			

The examples in Table VI and the above-described examples in which an n-butane feed was oxidized to maleic anhydride demonstrate that the novel catalyst compositions herein are useful as catalysts for the partial oxidation of a suitable hydrocarbon feed with molecular oxygen for the production of maleic or phthalic anhydride. Suitable hydrocarbon feeds include aromatic hydrocarbons containing up to 10 carbon atoms as exemplified by o-xylene and naphthalene and saturated or mono- or di-olefinic acyclic or cyclic hydrocarbons which have a carbon atom content in the range 4 to 10 and a linear chain of at least 4 carbon atoms.

The high surface phosphato-vanado mixed oxide complexes herein exhibit, in general, long catalyst lives and excellent retention of selectivity. After the initial breaking in of the activated catalyst, long periods of continuous use are indicated. Thus, over a period of 1200 hours on stream, a representative catalyst has been used without evidence of appreciable deactivation or loss of activity. Estimated useful lives for these catalysts exceed eight months and probably are sixteen months or more.

The fixed bed or fluid bed process conditions normally employed for the partial oxidation of a hydrocarbon feed are, in general, satisfactory for use with the high surface mixed oxides of the invention as follows:

CONDITION	RANGE
Temperature, °C.	300-500, preferably 325-490
Pressure, atm.	0.5-10, preferably 1-5
Contact time, sec.	0.05-5, preferably 0.1-2;

and a feed mixture, air plus hydrocarbon, or oxygen-containing gas plus hydrocarbon which is outside the explosive range.

In view of the exceptional activities of the high surface mixed oxides of the invention, they are especially effective for use as catalyst for the partial oxidation of n-butane. The oxidation conditions in this case desirably include a temperature in the range 350-490°C., preferably 375-475°C., and the other condition, as noted above. n-Butane-air feed mixtures which contain an amount of n-butane in the range 0.5 to 1.8 volumes per 100 volume of air are preferred feed mixtures for use in fixed bed reactors. In the case of fluid bed reactors, a more concentrated feed stream is satisfactory and the range of the hydrocarbon to air volume ratio may be as much as 0.5-10 to 100.

The mixed oxides of the invention may be sized as desired in the usual manner, grinding, screening and the like, and employed. They may also be comminuted, slurried in a suitable liquid medium, and extruded or pelleted as desired. Similarly, they may be comminuted, slurried in a suitable liquid medium with or without an ordinary binding agent and shaped as desired, for example in spheres, or disposed upon a suitable inert support such as alumina, titania, silicon carbide, silica, kieselguhr, pumice, and the like. Alternatively, the mixed oxide may be disposed upon an inert carrier by adding the carrier to a concentrate of the oxides in an essentially organic medium and evaporating the organic solvent.

The oxidation catalyst of the invention-whilst principally of use in the oxidation of n-butane to maleic anhydride, may also be used to oxidise a hydrocarbon feed selected from aromatic hydrocarbons containing up to 10 carbon atoms and saturated or mono- or di-olefinic acyclic or cyclic hydrocarbons having from 4 to 10 carbon atoms and a linear chain of at least 4 carbon atoms.

## WHAT WE CLAIM IS:-

1. A catalyst comprising a crystalline phosphorus-vanadium mixed oxide which comprises pentavalent phosphorus, vanadium and oxygen, the vanadium having an average valence in the range of from plus 3.9 to plus 4.6, said oxide having a phosphorus to vanadium atomic ratio in the range of from 0.9-1.8 to 1 and an intrinsic surface area in the range of from 7 to 50 square metres per gram. 5
2. A catalyst as claimed in claim 1, wherein the average valence of the vanadium is in the range of from 4.1 to 4.4, the phosphorus to vanadium atomic ratio is in the range of from 1.0-1.5 to 1 and the intrinsic surface area is in the range of from 10 to 50 square metres per gram. 10
3. A catalyst as claimed in claim 1 or 2, wherein the mixed oxide has a B-phase content of at least 25 percent. 10
4. A catalyst as claimed in claim 1 or 2, wherein the mixed oxide has a B-phase content in excess of 50 percent.
5. A catalyst as claimed in any preceding claim, wherein the mixed oxide is disposed upon an inert support. 15
6. A catalyst as claimed in claim 1, wherein the mixed oxide has a phosphorus to vanadium atomic ratio of 1.2 and an intrinsic surface area of about 23 square metres per gram.
7. A catalyst as claimed in claim 1 or 2, wherein at least 25 percent of the mixed oxide is composed of crystals having a unit cell of the dimensions  $a = b = 19.2 \text{ \AA}$  and  $c = 7.8 \text{ \AA}$ .
8. A catalyst as claimed in claim 7, wherein in excess of 50 percent of the mixed oxide is composed of said crystals. 20
9. A catalyst as claimed in claim 6, 7 or 8, wherein the mixed oxide is disposed upon an inert support.
10. A catalyst as claimed in claim 1 or 2, wherein the mixed oxide is composed of crystals exhibiting an X-ray powder diffraction pattern (Cuk $\alpha$ ), when mixed with  $\alpha$ -alumina in a 5 to 1 weight ratio of the mixed oxide to  $\alpha$ -alumina, in which the ratio of intensities of the  $d = 3.9 \text{ \AA}$  line to the  $d = 2.085 \text{ \AA}$  line of the mixture is at least 0.8. 25
11. A catalyst as claimed in claim 10, wherein said ratio of intensities is in excess of 1.6.
12. Process for preparing a catalyst as claimed in claim 1, which comprises reacting a vanadium oxide or precursor therefor and a phosphorus oxide or precursor therefor in an organic solvent medium in the absence of a gross amount of water in the medium to obtain a phosphorus-vanadium mixed oxide, the amounts of reactants used being such as to obtain in the mixed oxide a phosphorus to vanadium atomic ratio in the range of from 0.9:1 to 1.8:1, isolating the said mixed oxide from the organic solvent medium and activating the resulting mixed oxide by a heat treatment to obtain the required catalyst. 30
13. Process according to claim 21 wherein vanadium pentoxide and orthophosphoric acid are reacted in isobutanol. 35
14. Process in accordance with claim 12 for preparing a catalyst as claimed in claim 1, substantially as described with reference to any one of the foregoing Examples 1 to 13 and 15 to 17.
15. Process for producing maleic anhydride or phthalic anhydride, which comprises partially oxidizing a hydrocarbon feed in a molecular oxygen-containing atmosphere in the presence of a catalyst as claimed in any one of claims 1 to 11 to produce the required acid anhydride, the hydrocarbon feed being selected from aromatic hydrocarbons containing up to 10 carbon atoms and saturated or mono- or di-olefinic acyclic or cyclic hydrocarbons having from 4 to 10 carbon atoms and a linear chain of at least 4 carbon atoms. 40
16. Process according to claim 15, wherein the hydrocarbon feed is *n*-butane. 45
17. Process according to claim 15, wherein the hydrocarbon feed is benzene.
18. Process according to claim 15, wherein the hydrocarbon feed is *o*-xylene and the product obtained comprises predominantly phthalic anhydride.
19. Process according to claim 15, 16, 17 or 18, wherein the partial oxidation is effected at a temperature in the range of from 300 to 500°C. 50
20. Process according to claim 19, wherein the temperature is in the range of from 325 to 490°C.
21. Process according to claim 16, wherein the partial oxidation is effected at a temperature in the range of from 375 to 475°C. 55
22. Process according to any one of claims 15 to 21, wherein the oxygen-containing atmosphere is air.
23. Process for producing maleic anhydride, substantially as described with reference to any one of the foregoing Examples 21 to 30.
24. Process for producing phthalic anhydride, substantially as described with reference to the foregoing Example 31. 60
25. Maleic anhydride or phthalic anhydride whenever produced by the process claimed in any one of claims 15 to 24.



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